

## IV.B.3 Abuse Tolerance Improvements (SNL)

### OBJECTIVES

- Elucidate degradation mechanisms in lithium-ion cells that lead to poor abuse tolerance (runaway thermodynamics, gas evolution, electrolyte combustion)
- Develop and evaluate advanced materials (or materials combinations) that will lead to more abuse tolerant lithium-ion cell and battery systems
- Build 18650 cells in the SNL fabrication facility for cell level evaluation of new materials in support of all ABR thrust areas

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### TECHNICAL BARRIERS

There are several technical barriers to achieving the goals stated above including:

- Develop advanced material components designed to improve the intrinsic abuse tolerance of lithium-ion cells and do not lead to high order catastrophic failures
- Mitigate the gas evolution and decomposition of the electrolyte
- Passivation of cathode runaway reactions and interfacial reactions with electrolyte
- Limited quantities of advanced materials (and numbers of cells with new materials) to evaluate abuse response

### TECHNICAL TARGETS

- Quantify the thermal runaway response of materials at the cell level (18650)
- Determine the effect of high energy materials, electrolyte salts, solvents and additives on the abuse response of lithium-ion cells
- Determine the effect of advanced material components on the abuse response of lithium-ion cells
- Optimize electrochemical performance of new electrolyte components to meet DOE goals

### ACCOMPLISHMENTS

- Determined the thermal runaway response of high capacity LMR-NMC cathode materials
- Evaluated several advanced lithium-ion electrolytes to determine relative performance and abuse tolerance attributes
- Scaled the synthesis of LiF/ABA to the 1 kg scale (ANL MERF) and confirmed the performance of the scaled material
- Demonstrated the performance of LiF/ABA cells under overcharge and thermal abuse conditions

## INTRODUCTION

As lithium-ion battery technologies mature, the size and energy of these systems continues to increase (> 50 kWh for EVs); making safety and reliability of these high energy systems increasingly important. While most material advances for lithium-ion chemistries are directed toward improving cell performance (capacity, energy, cycle life, etc.), there are a variety of materials advancements that can be made to improve lithium-ion battery safety. Issues including energetic thermal runaway, electrolyte decomposition and flammability, anode SEI stability, and cell-level abuse tolerance continue to be critical safety concerns. This report highlights work with our collaborators to develop advanced materials to improve lithium-ion battery safety and abuse tolerance and to perform cell-level characterization of new materials.

## APPROACH

The effect of materials (electrolytes, additives, anodes, and cathodes) on the thermal response of full cells is determined using several techniques. One of the most useful and quantitative techniques is accelerating rate calorimetry (ARC). The ARCs at SNL are fitted with uniquely designed high pressure fixtures to not only measure quantitative energy release but also gas generation under ideal adiabatic conditions during full cell runaway. Cells were fabricated using a variety of active materials, electrolytes, and additives in the SNL cell prototyping facility. The in-house prototyping capability gives us the versatility to target candidate materials, perform full cell evaluation, and correlate cell response to fundamental materials properties.

Abuse testing is performed to determine the cell response to potential abuse conditions and document the outcomes including 1) failure point of energy storage device 2) conditions that cause failure 3) failure modes and 4) quantitate cell or module response to the abuse condition.

Our approach to developing advanced materials to improve abuse response focuses on redesigning lithium-ion cell electrolytes. This work starts with developing novel two-part electrolyte salts based on inherently stable lithium salts and anion binding agents (ABAs). The ABA components have two important design features: (1) improve the solubility of lithium salts in carbonate solvents by coordinating the salt negative ion at the electron withdrawing coordination site of the ABA and (2) passivate chemical decomposition reactions at electrode interfaces or in the bulk electrolyte to minimize the consequences and severity of thermal runaway and electrolyte combustion.

## RESULTS

### High Energy Materials

One objective for FY15 was to determine the baseline thermal runaway response of high energy LMR-NMC materials. While there is a great deal of interest in the LMR-NMC class of materials as high capacity alternatives to NMC, there is little known about the safety of LMR-NMC relative to conventional NMC. ARC was used to measure the cell-level thermal runaway of LMR-NMC cells and compare that behavior to other materials in cells. Figure 1 shows cell normalized heating rate and exotherm temperature for LMR-NMC/graphite, NMC 523/graphite, NMC 523/Si-C, NMC 111/graphite, and LFP/graphite cells. The LMR-

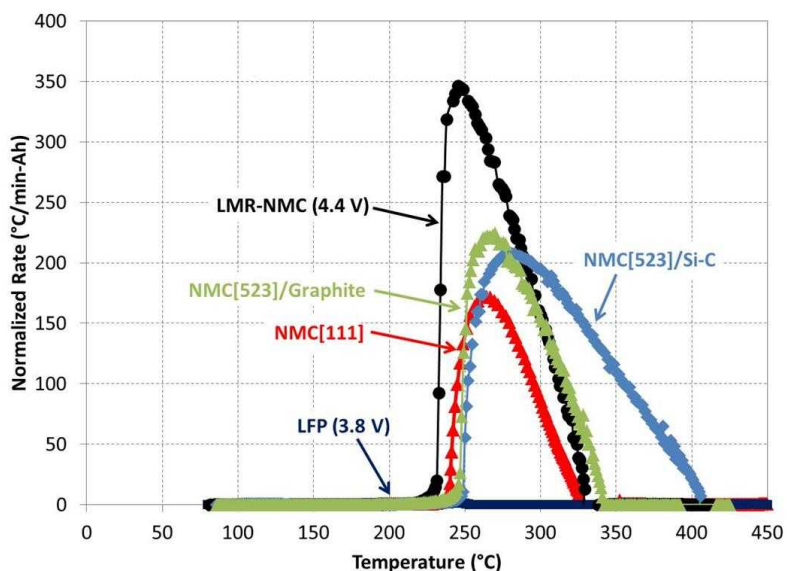


Figure 1: Normalized heating rate (°C/min) as a function of temperature measured by accelerating rate calorimetry (ARC) for LMR-NMC, NMC 523/graphite, NMC523/Si-C, NMC 111, and LFP 18650 cells.

NMC cell runaway shows the highest peak heating rate ( $\sim 350$  °C/min) relative to the other NMC cathode cells (175-225 °C/min). It is important to note that the LMR-NMC cell is measured at 4.4 V at 100% SOC, compared to 4.2 V for the NMC cells, which will contribute to the difference in the observed normalized heating rate. As a point of reference, the peak heating rate of the LFP/graphite cells (measured at 3.8 V at 100% SOC), is on the order of 1.5 °C/min. The total temperature rise during the runaway (related to the total heat release) is comparable for the NMC/graphite and LMR-NMC/graphite cells, but is significantly greater for the NMC/Si-C cell. This is attributed to more heat release at higher temperature during runaway for Si-C compared to graphite (determined by DSC measurements in FY14).

### Abuse Tolerance of Advanced Electrolytes

There are several recently developed electrolytes based on LiF, TFSI, ionic liquids, fluorinated ethers, phosphines, phosphazenes, and siloxanes that have one or more advertised abuse tolerant attributes including non-flammable, thermally stable, and high voltage (to 5 V vs. lithium). However, there has not been an independent, systematic studies of any of these electrolytes to study their safety attributes and any trade-offs with electrochemical performance. This work focuses on studying the electrochemical performance, cell thermal runaway reactivity, abuse tolerance, and flammability of these types of electrolytes in NMC/graphite cells.

The electrolytes studied and their intended attributes related to cell safety are provided in Table 1. The baseline electrolyte is 1.2 M LiPF<sub>6</sub> in EC:EMC (3:7). ABA electrolyte includes an alternative lithium salt based on LiF and a binding agent. FM2 contains a phosphazene additive. OS contains an organosilicon co-solvent. HFE is based on hydrofluoroether co-solvents. Compositions of ABA and HFE, developed at Sandia, are provided in Table 1. Compositions of the FM2 and OS electrolytes are not provided in this report. It is important to note that the quantities of each electrolyte component will dramatically impact their overall performance. All of this work presented is for one specific composition of each electrolyte type, with the exception of OS, where there are two formulations in this study (OS1 and OS2). Other compositions may give different performance than what is shown here.

**Table 1. Electrolytes evaluated for performance and abuse tolerance**

Electrolyte	Formulation	Intended Attributes
Baseline	1.2 M LiPF <sub>6</sub> in EC:EMC (3:7)	(Baseline)
ABA	1.0 M LiF/ABA + 2% VC	Mitigate thermal runaway severity, enhanced abuse tolerance
FM2	Proprietary	Flame retardant
OS	Proprietary	Enhanced thermal stability
HFE	1.0 M LiTFSI in EC:DEC:HFE (5:45:50)	Non-flammable, good electrochemical performance

Figure 2 shows the discharge capacity of  $\sim 1$  Ah NMC 523/graphite cells with the 5 electrolytes. The FM2, ABA, and baseline electrolytes have very consistent discharge capacities (measured at a C/5 discharge rate). OS1 and HFE electrolytes give slightly lower discharge capacities (5% less than the baseline), which could be attributed to the poorer ambient temperature conductivity of both OS1 and HFE relative to the baseline (Figure 3). Cycle life of each electrolyte in NMC 523/graphite cells was started in FY15 and some experiments are still in progress. Current results are shown in Figure 4 for the baseline, FM2 and ABA cells. The ABA cell shows 80% capacity retention at 200 cycles, while FM2 and baseline cells show 80% capacity retention at 260 and 300 cycles.

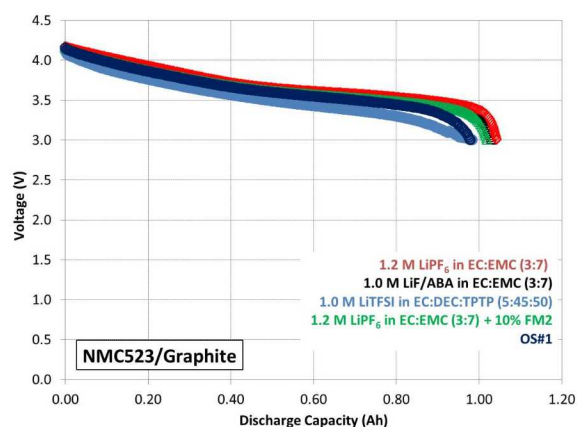


Figure 2. A plot of cell voltage and discharge capacity for NMC523 cells with different electrolytes

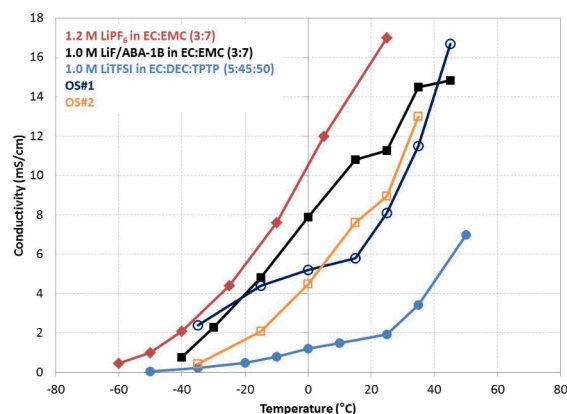


Figure 3. A plot of electrolyte conductivity vs. temperature for various electrolytes

The rate capability of each NMC/graphite cell with different electrolytes from C/10 to 2C is shown in Figure 5. Interestingly, the baseline OS1 electrolyte shows the best capacity retention at 2C, while having an ambient temperature conductivity that is only ~7 mS/cm (compared to >17 mS/cm for the baseline). This suggests that while the bulk liquid conductivity of the OS1 electrolyte is relatively low, the interfacial conductivity must be relatively high in order to give good rate capability. This behavior will be confirmed by complex impedance spectroscopy measurements.

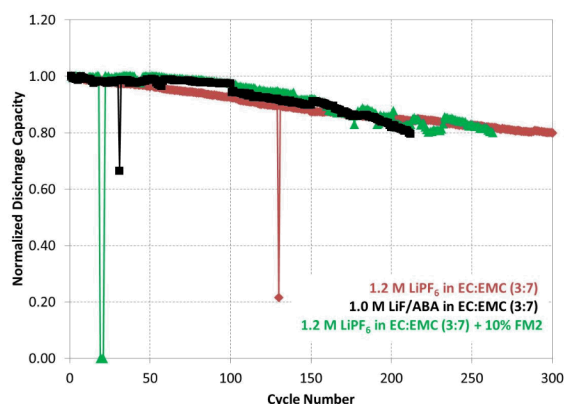


Figure 4. Normalized discharge capacity as a function of cycle number for NMC cells with various electrolytes

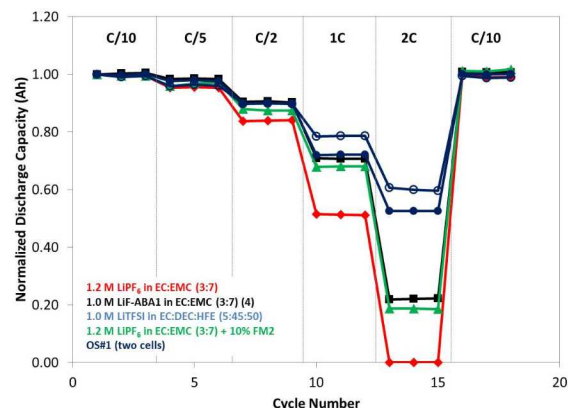


Figure 5. Rate capability plotted as normalized discharge capacity for discharge rates from C/10 to 2C.

Thermal runaway behavior of each of these electrolytes in NMC/graphite cells is evaluated by ARC. Figure 6 shows the normalized heating rate (°C/min) as a function of temperature during the exotherm region of the thermal runaway measured by ARC. The baseline cell has a runaway onset temperature of ~225 °C, a peak heating rate of ~200 °C/min and a total temperature rise of ~330 °C. The OS1, OS2, FM2 electrolytes all have similar thermal runaway behavior to the baseline cells. The two notably different performing cells are the HFE and ABA cells. The HFE cell has a significantly lower thermal runaway onset temperature of ~205 °C and a higher peak heating rate of ~300 °C/min relative to the baseline cell. While this could be attributed to the reactivity of the HFE electrolyte component, the DEC co-solvent may also play a role (note that the baseline cell is 70% EMC and the HFE cell is 45% DEC). The combustion enthalpy for DEC is 2715 kJ/mole and for EMC is 2000 kJ/mole, which could contribute to a lower onset temperature and a more energetic thermal runaway for the DEC containing HFE electrolyte relative to the EMC containing baseline cell.

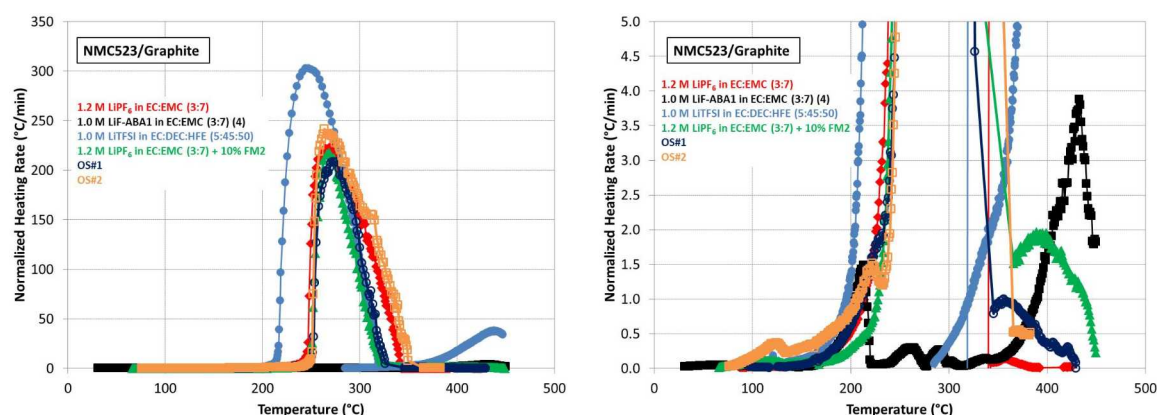


Figure 6. Normalized heating rate as a function of temperature for ARC measurements of NMC cells with different electrolytes (expanded view on the right side)

The thermal runaway reactivity of the ABA cell is significantly less than baseline cell (and all of the other cells in this study). The peak heating rate of the ABA cell is  $\sim 1.5$  °C/min and the entire high rate portion of the runaway is completely eliminated (shown in the expanded view of Figure 6). This is consistent with the behavior of ABA electrolytes in NMC cells reported in FY13 and 14, during the development of these electrolytes. Characterization studies of the mechanism of ABA behavior were initiated in FY15 in collaboration with the ANL CAMP facility and will continue in FY16. The ABA electrolyte is the only one in this series that exhibits a measureable improvement in NMC/graphite thermal runaway performance relative to the baseline.

In addition to the ARC measurements, the abuse tolerance of each of these electrolytes is also evaluated in NMC cells.

Figure 7 shows plots of cell voltage (dashed line) and temperature (solid line) as a function of %SOC for each of these cells during a 1C overcharge abuse test. The ABA cell reaches the compliance voltage at 160% SOC and the test is ended without the cell going into thermal runaway (peak temperature of  $\sim 120$  °C). All of the other cells exhibit an energetic failure at  $\sim 170$ -175 %SOC with peak temperatures as high as  $>400$  °C.

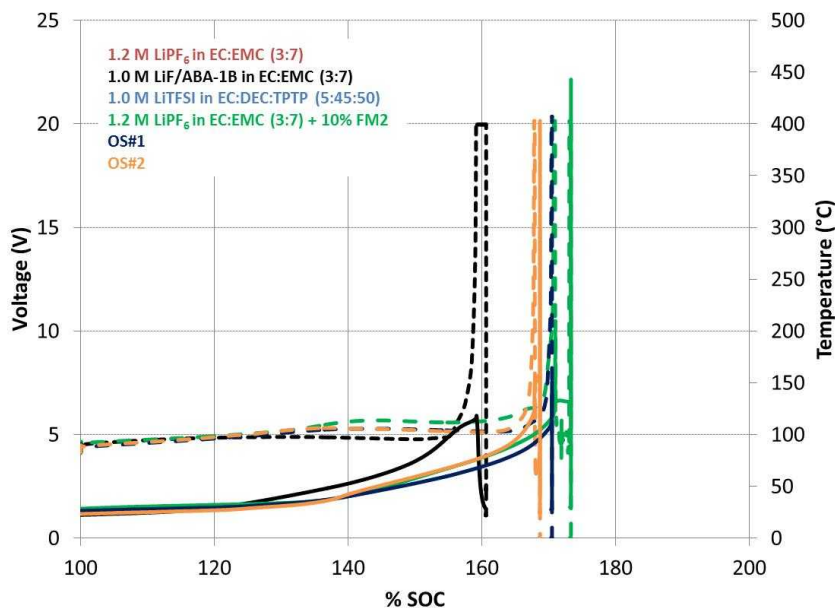


Figure 7. Cell voltage and temperature as a function of SOC during 1C overcharge testing of NMC cells with various electrolytes. measurements

Electrolyte flammability was measured by the approach developed at SNL and reported by Nagasubramanian et al.<sup>1</sup> Cells are heated until they vent directly into an ignition source to measure of electrolyte flammability during an actual cell vent failure. Figure 8 shows still images from the video of flammability tests of NMC cells with various electrolytes. All of the electrolytes tested ignite and sustain a fire for at least several seconds, with the exception of the HFE electrolyte which does not ignite or burn under these test conditions. At 50% HFE co-solvent, there is no ignition of this electrolyte during a cell vent. We have determined that the flammability of HFE electrolytes is somewhat variable at 30% HFE co-solvent, but have not done a systematic study through the co-solvent fractions. This suggests that in this co-solvent approach to non-flammable electrolytes, a significant fraction of non-flammable co-solvent needs to be used in order to achieve non-flammable characteristics of the blended electrolyte.

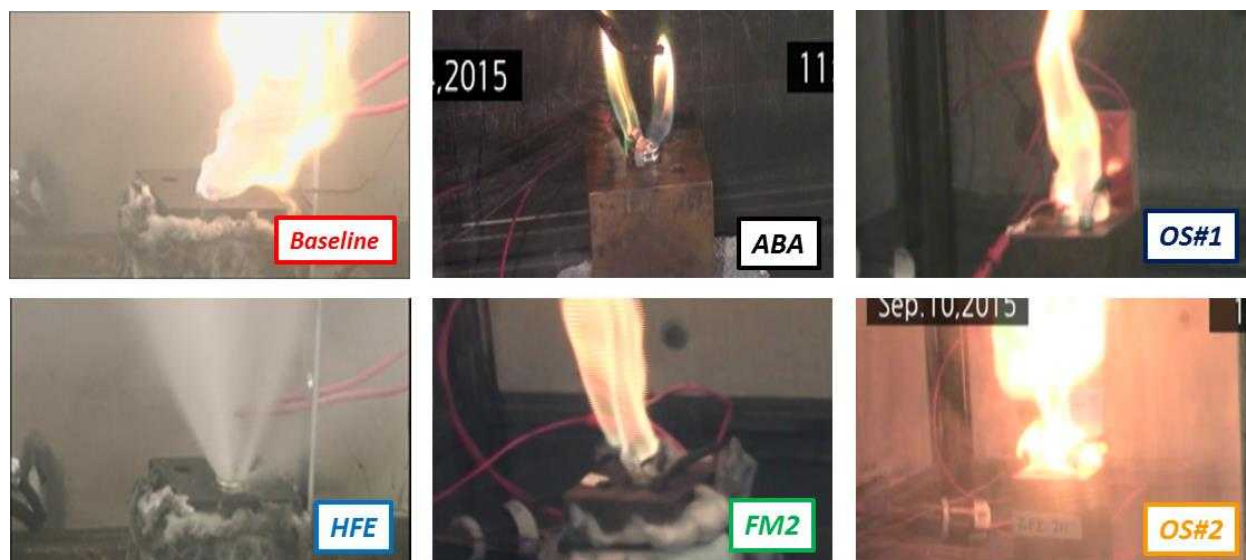


Figure 8. Still images during flammability tests of various electrolytes in NMC cells

## CONCLUSIONS AND FUTURE DIRECTIONS

This work demonstrates how specific advances in a variety of materials areas (anode, cathode, and electrolyte) can impact cell-level safety and thermal characteristics. We have reported on the thermal runaway properties of cells containing LMR-NMC cathodes to better understand how this class of high energy cathode materials will impact cell and battery-level safety and abuse tolerance. Results show the LMR-NMC cells to be kinetically more reactive than conventional NMC cells during thermal runaway. The magnitude of this change is expected given the higher cell voltage of LMR-NMC (4.4 V) relative to NMC (4.2 V). We have also evaluated the performance and safety of a series of lithium-ion battery electrolytes. Results show some improvement in the performance metrics with the advanced electrolytes, namely the rate capability of the OS electrolytes at 2C in spite of the fact that it exhibits lower bulk conductivity than conventional  $\text{LiPF}_6$  in EC:EMC electrolyte. Only the LiF/ABA electrolyte shows a benefit in the thermal runaway behavior and tolerance to overcharge of NMC cells relative to cells with the baseline electrolyte. Only the HFE electrolyte was shown to be non-flammable under cell vent test conditions (for the electrolyte that contains 50% HFE co-

<sup>1</sup> G. Nagasubramanian, C. J. Orendorff, "Hydrofluoroether electrolytes for lithium-ion batteries: Reduced gas decomposition and nonflammable" J. Power Sources, 196 (2011) 8604-8609.

solvent). Work will continue in develop a better understanding of the abuse response and thermal runaway behavior of high energy alloy anode and electrolyte materials for these electrolyte materials for lithium-ion and other advanced energy storage technologies.

#### **FY 2015 PUBLICATIONS/PRESENTATIONS**

1. C. J. Orendorff et al., “Quantifying Thermal Runaway by Battery Calorimetry and Opportunities for Improvement” IAPG Safety Panel, San Diego, CA, February 2015
2. J. Lamb et al. “Failure Propagation in Multi-Cell Lithium Ion Batteries” J. Power Sources 283 (2015), 517-523.
3. C. J. Orendorff et al., “Advancing Battery Safety through Materials Development and Testing” Next Generation Batteries 2015, San Diego, CA, April 2015
4. J. Lamb et al. “Safety Testing Challenges for Grid-Scale Energy Storage Systems” Next Generation Batteries 2015, San Diego, CA, April 2015.
5. J. Lamb et al., “Studies on the thermal breakdown of common li-ion battery electrolyte components” J. Electrochem. Soc., 162 (2015), A2131-A2135.
6. J. Lamb, et al., “Advances Toward Inherently Safe Lithium-Ion Batteries,” Advanced Automotive Batteries Conference (AABC) 2015, Detroit, MI, June 2015.